

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rsr

A review on microwave-assisted production of biodiesel

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ARTICLE INFO

Article history:

Received 27 December 2011

Received in revised form

19 March 2012

Accepted 31 March 2012

Available online 27 June 2012

Keywords:

Biodiesel

Transesterification

Microwave-assisted technology

ABSTRACT

Energy is the most important necessity for human existence on the earth. Limited crude petroleum resources and increasing awareness regarding the environmental impacts of fossil fuels are driving the search for new energy sources and alternative fuels. Biodiesel is a fuel which is renewable, biodegradable, environmentally friendly, and non-toxic in nature and has attracted considerable attention during the past decades. The costs of feedstock and the production process are two major hurdles to large-scale biodiesel production in particular. Various technologies have been developed to reduce the production cost. This paper attempts to extensively review microwave-assisted technology for biodiesel production. Additionally, different types of feedstocks for biodiesel production have been summarized in this paper. It is concluded that the microwave-assisted technique reduces the reaction time significantly in comparison with conventional methods. In addition, a high quality biodiesel can be obtained from microwave-assisted transesterification of different kinds of oils. Finally, the energy payback for 1 kg biodiesel produced by microwave-assisted technology is calculated in this paper and it indicated that the system is sustainable. Therefore it can be a suitable method of decreasing the cost of biodiesel and can also help the commercialization of this fuel.

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Nomenclature

CFPP	Cold filter plugging point
FFA	Free fatty acid
FAME	Fatty acid methyl ester
FAEE	Fatty acid ethyl ester
UCO	Used cooking oil
UCPO	Used cooking palm oil

WFPO	Waste frying palm oil
MEC	Microwave energy consumption
SEC	Stirrer energy consumption
TEC	Total energy consumption
TECPL	Total energy consumption per liter
TECPK	Total energy consumption per kilogram
BSFC	Brake specific fuel consumption
PE	Produced energy

1. Introduction

1.1. Overview of energy resources, production, and consumption in the world

Energy is a primary requirement in a human's life. It is known to be an important key input in most economic sectors such as food, industry, transportation, and agriculture as well as electricity generation [1,2]. Population growth plays an effectual role in the amount and type of energy use. Table 1 shows the compound average annual growth by region for OECD and non-OECD countries. Population growth declines gradually over the forecasted period from 1.1% per year in 2008–2020 to 0.7% in 2020–2035. It is estimated that the non-OECD population will rise from 5.5 billion in 2008 to 7.2 billion in 2035 with an annual average rate of increase of 1%. Thus these countries (mainly Asian and African) have an overwhelming effect on the global population. Russia is the only major non-OECD country whose population will fall from 142 million in 2008 to 126 million in 2035 and Africa faces the highest annual growth rate of 1.9% during this period. Although the growth rate for some nations is negative, the world population is forecasted to increase by an average rate of 0.9% per year from 6.7 billion in 2008 to 8.5 billion in 2035, as illustrated in Table 1 [3]. Economic growth is another important factor in the quality and quantity of energy use. It is found that the demand for energy tends to increase in line with gross domestic product (GDP), although usually at a lower rate. Between 2009 and 2011, the real GDP rose at the average rate of 2.4% per year [4].

The total annual crude oil production in the world increased from 53.97 in 1985 to 73.68 (million barrels per day) in 2010 with

an average annual rate of increase of 0.7% between 2000 and 2010, as illustrated in Fig. 1. The total annual petroleum production in the world grew from 57.91 in 1985 to 82.43 (million barrels per day) in 2010 with an average annual rate of increase of 1.0% between 2000 and 2010. On the other hand, the total annual petroleum consumption in the world increased from 60.09 in 1985 to 85.26 (million barrels per day) in 2010 with an average annual increase of 1.1% between 2000 and 2010. Due to the acquirement by refineries of materials including alcohol and liquid products produced from coal and other sources, total petroleum consumption is higher than its production and is growing at a higher rate. Table 2 illustrates the total oil reserves, production, and consumption in the world, the USA, and OPEC in 2009. Presently, fossil-fuel-based energies such as liquid fuels, natural gas, and coal are the major sources of energy in the world, and their consumption and consequently their production are rising sharply each year. Thus, the total fossil fuel reserves in the world are declining at the same rate, which will cause energy shortages in the future [5–7].

Recently fossil fuel combustion has become known as the main reason for climate change and global warming. Annual production of CO₂ emissions has increased dramatically in recent years. Carbon intensity of energy supplies and energy intensity of economic activities are two key factors that affect the level of

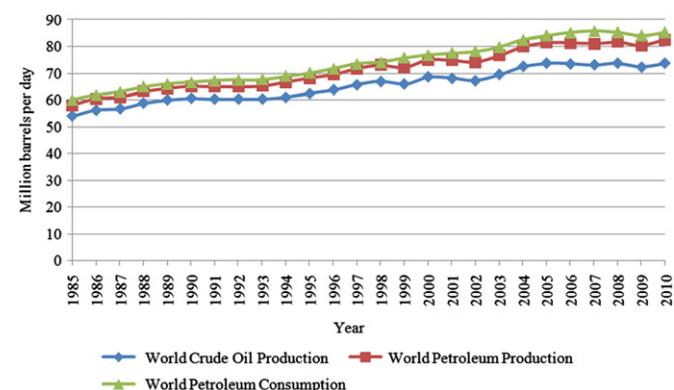


Fig. 1. World crude oil consumption and petroleum consumption and production.

Table 1

Population growth by region (compound average annual growth rates).
Source of data [3].

Region	1980–1990 (%)	1990–2008 (%)	2008–2020 (%)	2010–2015 (%)	2020–2035 (%)	2008–2035 (%)
OECD	0.80	0.70	0.50	0.50	0.30	0.40
North America	1.20	1.20	0.90	0.90	0.60	0.70
United States	0.90	1.10	0.90	0.90	0.60	0.70
Europe	0.50	0.50	0.30	0.40	0.10	0.20
Pacific	0.80	0.40	0.00	0.10	-0.30	-0.10
Japan	0.50	0.20	-0.20	-0.20	-0.60	-0.40
Non-OECD	2.00	1.50	1.20	1.20	0.80	1.00
E. Europe/Eurasia	0.80	-0.2	-0.1	0.00	-0.20	-0.20
Caspian	n.a.	0.80	1.00	1.00	0.60	0.70
Russia	n.a.	-0.20	-0.40	-0.30	-0.50	-0.40
Asia	1.80	1.40	1.00	1.10	0.60	0.80
China	1.50	0.90	0.60	0.60	0.10	0.30
India	2.10	1.60	1.20	1.30	0.70	1.00
Middle East	3.60	2.30	1.80	1.80	1.30	1.50
Africa	2.90	2.50	2.20	2.20	1.70	1.90
Latin America	2.00	1.50	1.00	1.00	0.60	0.80
Brazil	2.10	1.40	0.70	0.80	0.30	0.50
World	1.70	1.30	1.10	1.10	0.70	0.90
European Union	n.a.	0.30	0.20	0.20	0.00	0.10

Table 2

World oil reserves, production, and consumption in 2009 [5].

Region	Crude oil reserves (billion barrels)	Petroleum production (million barrels per day)	Petroleum consumption (million barrels per day)
United States	20.7	7.3	18.8
OPEC	946	33.7	8.9
Rest of world	375.9	39.5	56.7
Total	1342.6	80.5	84.4

carbon dioxide emissions. CO₂ emissions differ by energy source, but as long as fossil-fuel-based energies such as coal, liquid fuels, and natural gas are the main suppliers of energy in the world and their consumption is continuously increasing, production of carbon emissions will increase day by day. On the other hand, energy consumption per unit of economic activities, as measured by GDP, is increasing, which accelerates production of carbon emissions as well. According to projected data, CO₂ emissions will increase from 30.2 billion metric tons in 2008 to 35.2 billion metric tons in 2020 and 43.2 billion metric tons in 2035. Non-OECD and OECD countries accounted for about 73% and 6% of the total CO₂ emissions in 2008, respectively [8].

The limited supply of fossil-based resources, yearly increases in prices of fossil fuels, increasing demand for energy due to rises in the population growth rate and GDP, and finally climate change, global warming, and the growing rate of carbon emission have stimulated interest in finding new alternative and cheap energy resources. These resources comprise alternative energies such as solar, wind, hydro, and biomass [9]. Vegetable oils and animal fats appear to be potential resources for production of petroleum-based diesel fuel, namely biodiesel. It is a fuel which is renewable, biodegradable, environmentally friendly, and non-toxic in nature [10]. The environmental benefits of biodiesel make it more attractive as a suitable alternative and valuable substitute for petroleum-based diesel fuel. It has a remarkable potential to be a part of a sustainable energy mix in the future, especially in the transportation sector [11,12]. Biodiesel demand in European countries was expected to increase to 10.5 billion liters by 2010 [13]. Fig. 2 illustrates the total biodiesel production (in thousands of barrels per day) between 2000 and 2010. Biodiesel production increased from 15,200 barrels per day in 2000 to 335,700 barrels per day in 2010, with an average annual growth rate of 32.5% [14].

The costs of feedstock and the production process are two important factors which are particular obstacles to large-scale biodiesel production. The cost of feedstock can be tackled by using waste vegetable oil, which is considered a potential alternative feedstock for biodiesel production [15]. First, in comparison with edible oils, it does not compete with food production or divert agricultural products away from crops and second, in comparison with some of the non-edible oils, it does not have the cost of production and planting [16]. Recently, the microwave irradiation technique has been introduced as a well-established, economic, and energy efficient method of expediting the chemical reactions [17]. It can be a solution to overcome the cost of the production process. This study focuses on reviewing the microwave-assisted production of biodiesel as an attempt to reduce the energy requirements of this process.

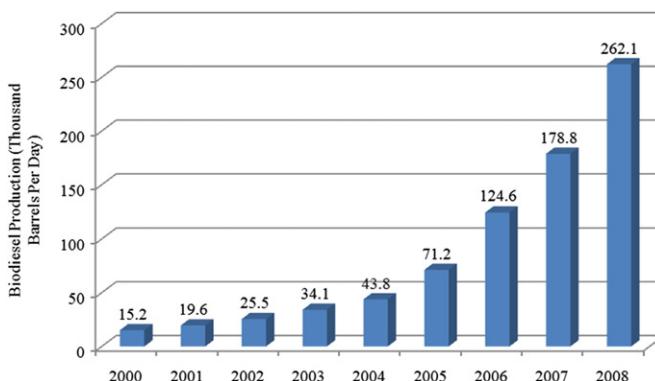


Fig. 2. Total world biodiesel production (thousands of barrels per day) between 2000 and 2008.

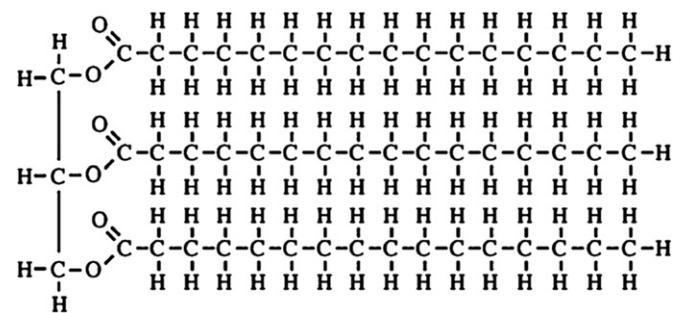


Fig. 3. Chemical structure of triglyceride molecule [19].

1.2. Triglycerides as engine fuels

Vegetable oils and animal fats are prominent candidates as alternative diesel fuels. The chemical structure of triglycerides, which consist of 98% triglycerides and small amounts of mono- and diglycerides, is illustrated in Fig. 3. The inventor of the diesel engine, Rudolf Diesel, tested peanut oil in his compression ignition engine for the first time during the World Fair in Paris in 1900 [18]. Vegetable oils were then used as fuel in diesel engines in the 1930s and 1940s but did not become commercialized because of the low price of petroleum products. Energy crises in the late 1970s and early 1980s as well as accompanying increases in the price of crude oil, depletion of fossil fuels, and environmental concerns renewed the interest in triglycerides as engine fuels.

Many problems due to direct ignition of vegetable oils are reported such as high viscosity, incomplete combustion, high carbon deposits, low volatility, and high cloud, pour, and flash points [20–22]. They are mainly associated with the large triglyceride molecule and its higher molecular mass, but these problems can be relieved by modification of vegetable oils to biodiesel [23–25].

1.3. Biodiesel

Biodiesel is defined as a clean burning mono alkyl ester of long chain fatty acids derived from natural, renewable feed stock, such as vegetable oil or animal fats, for use in compression ignition engines [26]. Vegetable oils have to be modified to be a suitable substitute for petroleum diesel and can be ignited in diesel engines. There are four major techniques to modify vegetable oils: dilution, microemulsion, pyrolysis (thermal cracking), and transesterification, which are used to reduce the viscosity [27]. Transesterification is the key input method for production of an environmentally friendly and safe fuel from unprocessed vegetable oils [22].

Biodiesel is a fuel which is renewable, biodegradable, environmentally friendly, and non-toxic in nature and can be used in normal diesel engines with good performance and even without any engine modification [28]. Besides, the environmental benefits of this fuel in comparison with normal fossil-based fuels like diesel have made it more attractive recently. In the USA and some of the European countries biodiesel is produced commercially and also consumed commonly in order to reduce air pollution and decrease dependence on fossil-based fuel [29]. Biodiesel is compatible with convention diesel and the two can be blended in any proportion to create a stable biodiesel blend. Thus, biodiesel has become one of the most common types of biofuels in the world.

2. Biodiesel as a potential renewable energy resource

2.1. Biodiesel feedstock

Alternative diesel fuels such as biodiesel can be produced from a wide variety of feedstocks. Selecting the best feedstock

according to the geographical location, climate, local soil condition, and agricultural practice of each country is vital to reduce the cost of biodiesel production [1]. Generally biodiesel feedstocks can be classified into four major groups as below:

- Virgin edible vegetable oils such as soybean, rapeseed, palm, sunflower, and coconut oils
- Non-edible oils such as Jatropha, karanja, neem, castor, tall, sea mango, and algae oils
- Waste vegetable oils
- Animal fats such as yellow grease, tallow, lard, chicken fat, and fish oil

Vegetable oils and animal fats are considered to be an inexhaustible renewable source of energy with an energy content close to that of diesel fuel. Recently they have become more attractive due to their environmental benefits. More than 350 oil-bearing crops have been identified; among them soybean [30,31], palm [32], sunflower [33,34], safflower [35], cotton seed [36], rapeseed [37], and canola [38] oils are considered the most commonly used potential feedstocks for biodiesel production [39,40]. However, some other non-edible and waste cooking oils have the potential to serve as raw material for biodiesel production [15,16]. Table 3 summarizes all the sources of feedstocks for biodiesel production including edible and non-edible oils, animal fats, and other biomass resources. Soybeans are commonly used in the USA, which has led to soybean biodiesel becoming the primary source of biodiesel in this country [41,42]. In Malaysia and Indonesia palm oil is used as a significant biodiesel source [43]. In the EU/Europe, rapeseed and sunflower oils are the feedstocks most commonly used in biodiesel production [42]. In India and Africa, the Jatropha tree is used as a significant fuel source [44]. Canola [45,46], coconut [47], linseed [48], cottonseed [48], and waste cooking oils [49] have been used in western

Canada, the Philippines, Spain, Greece, and China for biodiesel production, respectively.

2.2. Biodiesel policies and standards

Biodiesel production has been implemented across the world, especially in the EU, the USA, and some Asian countries. Production increased at an average annual growth rate of 30% between 2000 and 2008 and it is forecasted to increase at a higher rate during the next years. Many policies have been developed all around the world to allow the use of biodiesel fuels in countries' energy mixes and set targets for future biodiesel consumption. Pollution reduction, increasing job opportunities in rural sectors, and reduction of dependence on diminishing fossil fuel supplies are some other important goals which are driving many countries to produce biodiesel [14,51]. Table 4 summarizes some of the biodiesel targets in some selected countries.

The properties of biodiesel fuel produced vary with its production feedstocks; those countries that have adopted biodiesel have set their own specifications for biodiesel. These properties play a vital role in quality control in the petroleum-based fuel industry. The parameters which define the quality of biodiesel can be divided into two groups. One group contains major parameters such as density, viscosity, flash point, CFPP, pour point, cetane number, neutralization number and Conradson carbon residue, which are also used for mineral oil-based fuel, and the other group describes in particular the chemical composition and purity of fatty acid alkyl esters like the mass of alcohol, ester content, monoglycerides, diglycerides, triglycerides, and free and total glycerol in the biodiesel produced [2]. Among all the biodiesel standards, the American Standard Specification for Biodiesel (ASTM D 6751-02) and the European Standard for Biodiesel (EN 14214) are the two major biodiesel standards which are followed all over the world. Table 5 lists the ASTM D 6751 and EN 14214 biodiesel specifications in detail.

2.3. Advantages and disadvantages of biodiesel

Biodiesel can be considered as a new and clean replacement for diesel fuel. Using biodiesel as fuel has some advantages and disadvantages.

The following are some advantages of using biodiesel:

- It is a biodegradable, non-toxic, environmentally friendly, and renewable resource.

Table 3

Biodiesel feedstocks.

Source of data [50].

Worldwide biodiesel targets.

Source of data [16,51–66].

Country	Biodiesel targets
EU	Using 2% in 2005 and increasing in stages to a minimum of 5.75% by the end of 2010 and 20% by 2020
Japan	5% blend for biodiesel by 2010
Malaysia	Processed palm oil blend of 5%
Philippines	Coconut blend of 2% by 2009
Thailand	5% mix in 2007, 10% by 2011 and production of 8.5 million L per day by 2012
Brazil	Maximum blending of 3% biodiesel into diesel by July 2008 and 5% by end of 2010
Canada	2% renewable content in diesel fuel by 2012
India	Meet 20% of the diesel demand beginning in 2011–2012
Taiwan	Direct subsidies or other tax exemptions for biodiesel
China	Tax exemption for biodiesel produced from animal fats and vegetable oils

Edible oils	Non-edible oils	Animal fats	Other resources
Soybeans	Almond	LArd	Bacteria
Rapeseed	<i>Abutilon muticum</i>	TAallow	Algae
Canola	Andiroba	Poultry fat	Fungi
Safflower	Babassu	Fish oil	Micro algae
Barely	<i>Brassica carinata</i>		Tarpenes
Coconut	<i>B. napus</i>		Latexes
Copra	Camelina		Cooking oil (yellow grease)
Cotton seed	Cumaru		Microalgae (chlorella vulgaris)
Groundnut	<i>Cynara cardunculus</i>		
Oat	<i>Jatropha Ccurcus</i>		
Rice	<i>Jatropha nana</i>		
Sorghum	Jojoba oil		
Wheat	<i>Pongamia glabra</i>		
Winter rapeseed oil	Laurel		
	Lesquerella		
	fendleri		
	Mahua		
	Piqui		
	Palm		
	Karang		
	Tobacco seed		
	Rubber plant		
	Rice bran		
	Sesame		
	Salmon oil		

Table 5

Biodiesel specification parameter limits for B100 (ASTM 6751-02 and EN 14214). Source of data [16, 50, 53, 54, 67–73].

Properties	ASTM 6751-02	EN 14214
Density at 15 °C	870–890 kg/m ³	860–900 kg/m ³
Flash point	130 °C minimum	> 101 °C (minimum)
Viscosity @ 40 °C	1.9–6.0 mm ² /s	3.5–5.0 mm ² /s
Sulfated ash	0.020% m/m maximum	0.02% m/m (maximum)
Cloud point	Report to customer	Based on national specification
Copper strip corrosion	Class 3 maximum	Class 1 rating
Cetane number	47 (minimum)	51(minimum)
Water content and sediment	0.050 (%v) maximum	500 mg/kg (maximum)
Acid number	0.50 mg KOH/g maximum	0.50 mg KOH/g (maximum)
Free glycerin	0.02% (m/m) maximum	0.02% (m/m) (maximum)
Total glycerol	0.24% (m/m) maximum	0.25% (m/m)
Methanol content	0.20% (m/m) maximum	0.20% (m/m) (maximum)
Phosphorus	10 mg/kg maximum	10.0 mg/kg (maximum)
Distillation temperature	360 °C	–
Sodium and potassium	5.00 ppm maximum	5.00 mg/kg (maximum)
Oxidation stability	3h minimum	6 h (minimum)
Carbon residue	0.05 maximum wt%	0.30%(m/m) (maximum)
Calcium and magnesium	5 ppm maximum	5 ppm (maximum)
Iodine number	–	120 _{iod} /100g (maximum)

- It can reduce the amount of greenhouse gas emissions and it emits less CO₂, SO₂, CO, HC, and PM in comparison to conventional diesel.
- Production of biodiesel is easier than production of diesel fuel and it creates a brand new job infrastructure and will help local economies.
- It decreases the vibrations, smoke, and noise produced.
- The energy security of the country will be increased and there can be a reduction in fossil fuel use.
- Biodiesel is more cost efficient because it is produced locally.
- Biodiesel has a high flash point, which makes it a safer fuel.
- It does not need engine modification up to B₂₀.

On the other hand, there are several concerns about biodiesel:

- It emits higher NO_x emissions in comparison with conventional diesel.
- Its higher pour and cloud points create problems in cold weather.
- It has a corrosive nature against copper and brass.
- It has a higher viscosity in comparison with diesel fuel.
- It has low volatility.

An extensive summary of advantages and disadvantages of biodiesel as a substitute for conventional diesel can be found in Refs. [12,50,57,67,69,70,72,74–77].

3. Transesterification

3.1. Transesterification reaction

Transesterification (also called alcoholysis) is the well-established chemical reaction of vegetable oils and animal fats with an alcohol to form fatty acid alkyl esters and glycerol [78]. Neat vegetable oils and animal fats cannot be used directly in diesel engines because of their high viscosity and low volatility, and the major objectives of transesterification are to overcome these

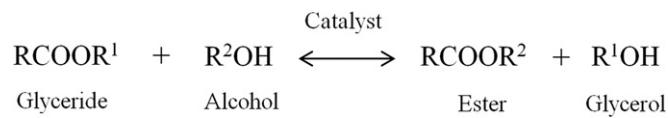


Fig. 4. General equation of transesterification.

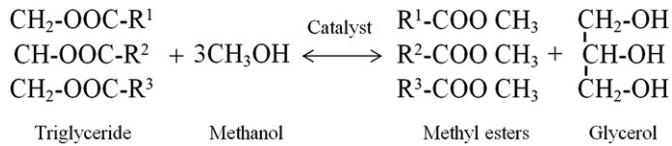


Fig. 5. General equation for transesterification of triglyceride in the presence of methanol.

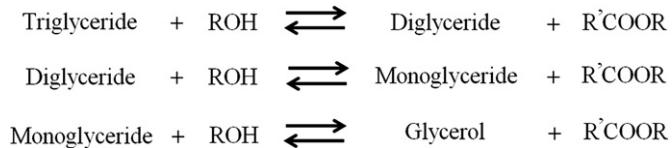


Fig. 6. The three reversible and consecutive reactions in the transesterification of triglyceride.

problems [79]. A 3:1 M ratio of alcohol to oil (stoichiometrically) is required to complete the reaction; however, since the reaction is reversible, the excess alcohol is practically used to shift the equilibrium to the product side and raise the product yield [21,23].

Methanol and ethanol are the most common alcohols used in transesterification, especially methanol due to its physical and chemical advantages (polar and shortest chain alcohol) and its low cost [80]. In addition a catalyst is normally used to accelerate the reaction and improve the conversion yield. Base, acid, and enzyme are three types of catalyst which are usually used in the transesterification reaction. This reaction is represented by the general equation in Fig. 4. If methanol is used in this process it is called methanolysis. Methanolysis of triglyceride is shown in Fig. 5.

3.2. Chemistry of transesterification reaction

The transesterification reaction consists of a sequence of three reversible consecutive reactions. In the first step, triglycerides are converted to diglycerides; in the second, diglycerides are converted to monoglycerides. In the last step, monoglycerides are converted to glycerol [50,81]. Three esters are obtained from one triglyceride molecule, one ester molecule for each glyceride at each step. The kinetics and mechanism of transesterification have been described in Refs. [22,23,82,83]. The basic mechanism is shown in Fig. 6.

4. Biodiesel production via transesterification reaction

4.1. Biodiesel production technologies

Several methods for production of biodiesel have been developed by scientists. In these methods, the transesterification process is carried out in the presence and absence of catalyst. The catalyst is applied to accelerate the reaction and produce biodiesel with higher quality. Alkaline, acid, and enzyme catalysts have been used depending on the characteristics of feedstock. The use of each catalyst has some advantages and disadvantages. The alkaline catalysts are preferable in terms of their lower reaction temperature, higher reaction speed (lower reaction time), and higher conversion efficiency in comparison with the acid catalysts

[30,39,84,85]; however acid catalysts are insensitive to FFA and are better than the alkaline catalysts for vegetable oils with FFA greater than 1% [80,86]. The transesterification reaction can also be carried out by using enzyme catalysts, which look attractive and encouraging for reasons of easy product separation, purification, washing, and neutralization. They can also be applied to high FFA feedstock, but the problems associated with enzyme catalysts are their higher cost and longer reaction time [78].

In all these methods, the transesterification process is carried out by using conventional heating. In conventional heating, heat energy is transferred to the reaction mixture through convection, conduction, and radiation from the surface of the reactor. Thus, in conventional heating, a large amount of the energy is needed to heat the media, which makes this method inefficient. In addition, a long reaction time (30 min to 8 h) is required to obtain a satisfactory conversion of oil (up to 95%) [87–92]. The conventional heating transesterification methods are reviewed and summarized in Refs. [2,27,93–95].

Other emerging technologies for the transesterification process are supercritical and ultrasound-assisted methods. In the supercritical method, alcohol acts as a solvent and acid catalyst as well [96]. The use of supercritical alcohol for biodiesel production of vegetable oil is investigated in Refs. [37,97–102]. Ultrasound is known as a method to enhance reaction rates. It has been proved that ultrasound technology improves the conversion yield significantly. The effect of using ultrasound technology in production of biodiesel is reported in detail in Refs. [103–107].

4.2. Microwave-assisted transesterification process

Microwave irradiation is an electromagnetic irradiation in the range of wavelengths from 0.01 to 1 m and corresponding frequency range of 0.3 to 300 GHz. Generally radar transmissions use the wavelengths between 0.01 and 0.25 m and telecommunications use the remaining wavelengths. All microwave reactors for chemical synthesis and all domestic microwave ovens operate at 2.45 GHz frequency, which corresponds to a wavelength of 12.25 cm. This is in order to avoid any interference with telecommunications and cellular phone frequencies. The microwave region of the electromagnetic spectrum is shown in Fig. 7. As indicated in this figure, this region lies between the infrared and radio frequencies [108].

Microwave irradiation is a well-established method of accelerating and enhancing chemical reactions because it delivers the energy directly to the reactant. Therefore, heat transfer is more effective than in conventional heating and the reaction can be completed in a much shorter time [17]. Thus microwave irradiation is one of the best methods of reducing the reaction time and

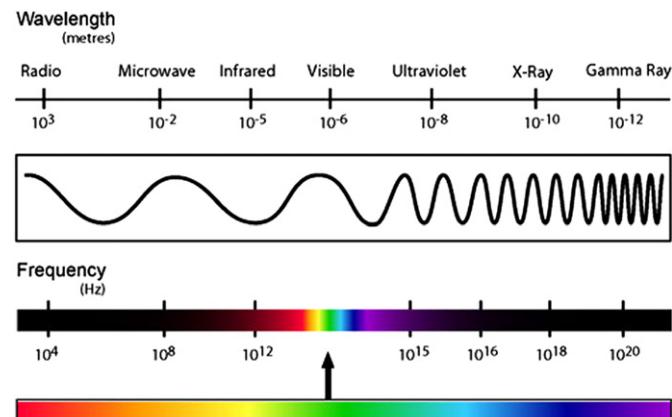


Fig. 7. The electromagnetic spectrum.

obtaining higher yields in the production of biodiesel. It enhances the speed of the reaction and makes the separation process easier in comparison with conventional heating. In this section, microwave-assisted biodiesel production has been reviewed extensively.

Lertsathapornsuk et al. reported a reduction in reaction time when using microwave irradiation to produce biodiesel from used cooking oil. Two important parameters, the molar ratio of ethanol to oil and the reaction time, vary in this study. The molar ratio of ethanol to oil varied from 3:1 to 18:1 and the reaction time varied from 10 to 100 s. The optimum condition for this conversion was 1.0% (wt/v) sodium hydroxide (NaOH) as the catalyst with a 9:1 M ratio and a reaction time of 10 s. The reaction time was reduced significantly [109].

Mazzozhia et al. transesterified the triglycerides to fatty acids methyl esters (FAMEs) in the presence of heterogeneous catalyst by using the microwave irradiation heating technique. Firstly it was observed that the microwave technique decreased the reaction time significantly, and secondly KSF montmorillonite was proven to be a promising catalyst for microwave-assisted production of biodiesel. It can work at a temperature of about 170 °C and can lower the alcohol to oil molar ratio (i.e., 9:1) in comparison with other heterogeneous catalysts [110].

Saifuddin and Chua investigated the effect of using microwave irradiation to enhance the production of biodiesel from UCO. First, the two-step transesterification followed by separation and washing was carried out under these reaction conditions: NaOH (0.5% and 1.0% by weight of oil) was selected as the catalyst with a 6:1 M ratio of ethanol to oil at room temperature and six different reaction times (3, 15, 30, 45, 60, and 75 min). Then, for comparison with this conventional method, the microwave irradiation method was used: 750 W output power was used to irradiate the reaction mixture. The experiments were repeated at 50% and 75% of exit power for all five different reaction times of 1–5 min. It was concluded that microwave irradiation greatly reduced the reaction time and ameliorated the conversion yield, which means that microwave irradiation is a fast and enhanced alternative to the normal conventional heating process. Also in this study the researchers used microwave irradiation in the washing process. It was obvious that microwave irradiation greatly speeded up the separation in the washing process [111].

Lertsathapornsuk et al. studied the preparation of FAEE from three types of oil: coconut oil, rice bran oil, and used frying palm oil. An 800 W modified microwave oven was used in their study. The best conversion yield was obtained by applying 1.0% NaOH as a catalyst with an alcohol to oil molar ratio of 9:1 for 30 s. Conversion yields of 100%, 94%, and 83% were obtained within 30 s for coconut oil, rice bran oil, and used frying palm oil, respectively. When the reaction time increased to 60 s, the conversion of used frying palm oil increased slightly but it did not do so for rice bran oil [112].

A fast and easy method for preparation of biodiesel from triolein under microwave irradiation was reported by Leadbeater and Stencel. The highest yield of biodiesel (98%) was obtained using 5% KOH or NaOH, a 6:1 M ratio of methanol to oil, and a reaction temperature of 323 K for 1 min under 25 W microwave exit power on batch scales of up to 3 kg of oil each time [113].

Microwave technology was used in the transesterification of cottonseed oil in the presence of methanol and potassium hydroxide by Azcan and Danisman. A Start S model microwave unit (Fig. 8) was used for the transesterification process in this study. Critical reaction parameters such as the amount of catalyst, reaction time, and reaction temperature were investigated to determine the optimum conditions in the conventional and microwave irradiation methods. High conversion yields of biodiesel in the range of 89.5–92.7% were obtained at the same reaction temperature of 333 K and catalyst–oil ratio of 1.5% for



Fig. 8. Start S microwave unit.

both methods while 30 min reaction time using conventional heating was decreased to 7 min by using the microwave irradiation technique [114].

The preparation of FAMEs in the presence of homogeneous catalysts (methyl *t*-butyl ether) under microwave irradiation was carried out by J. Hernando et al. The transesterification was done using either commercial rapeseed or soybean oil. A small scale batch microwave reactor and a microwave flow system were used to perform the experiment. In both of them a very high conversion yield of 97% was obtained in 1 min. It was concluded that using modern commercial devices allows a straightforward transfer of the process from batch to stop-flow [115].

Continuous preparation of biodiesel using the microwave irradiation method has been studied by Barnard. M et al. The transesterification reactions were performed by using a multimode microwave apparatus (CEM MARS) as shown in Fig. 9. The designed cycle can be used for new or used vegetable oils with a methanol to oil molar ratio of 6:1. The results showed a 97.9% overall conversion with a flow rate of 2 L/min and a 98.9% overall conversion with a flow rate of 7.2 L/min. In this study, it was suggested that continuous microwave irradiation production of biodiesel is more energy efficient than conventional heating and batch microwave heating. The energy consumption values (KJ/L) for conventional heating, microwave continuous flow at a flow rate of 7.2 L/min, microwave continuous flow at a flow rate of 2 L/min, and batch microwave heating of 4.6 L were 94.3, 26.0, 60.3, and 90.1, respectively [116].

Lertsathapornsuk et al. reported on a modified process for the transesterification of waste frying palm oil (WFPO). A schematic diagram of the modified continuous microwave reactor is shown in Fig. 10. The reaction conditions of the new process were 3.0% (by weight of oil) NaOH as the catalyst with a 12:1 M ratio of



Fig. 9. Multimode microwave apparatus (CEM MARS).

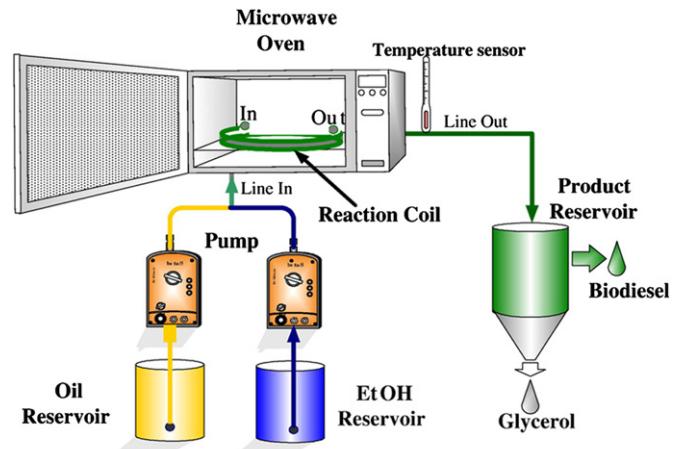


Fig. 10. Schematic diagram of the modified continuous microwave reactor.

ethanol to oil and 30 s reaction time. Thus, the NaOH concentration in the new process was increased to 3.0% to overcome the high percentage of FFA in the UCPO. In this experiment one part of NaOH was used to neutralize the UCPO and the rest was applied as the catalyst in the process. With this new method the conversion of UCPO was increased to 97% [117].

The high oil content (40%) of rapeseed makes it an important source of vegetable oil. The transesterification of rapeseed oil using methanol as the alcohol and KOH and NaOH as the alkaline catalysts was studied by Azcan and Danisman. The catalyst ratio (0.5%, 1%, and 1.5% (wt./wt.)), reaction temperature (313, 323, and 333 K), and reaction time (1, 3, and 5 min) were the investigated effective reaction parameters in this research. The high percentages of the obtained yield (88.3–93.7%) and purity (87.1–99.4%) and the short reaction times indicated the high efficiency of microwave irradiation for the production of biodiesel. The highest yield in this study (93.7%) took place under the following reaction conditions: first, 313 K, 1 min reaction time, and 1.0% KOH; second, 323 K, 5 min, and 1.0% KOH [118].

Reefat et al. studied the production of biodiesel by using the microwave irradiation method. The optimum parametric

conditions used in their study were obtained from the conventional technique to compare microwave irradiation with conventional techniques. The temperature was 65 °C, a molar ratio of 6:1 (methanol/oil) was used, and 1.0% (by weight of oil) KOH was employed for this transesterification process. The results indicated that use of microwave irradiation made the production of biodiesel very fast (2 min) compared with the conventional technique (60 min) under the same optimal reaction conditions and also increased the yield to 100% [119].

The method of preparation of FAME from *Jatropha Curcas* oil in a microwave oven has been investigated by Yaakob et al. The maximum biodiesel conversion of 86.3% was obtained in an excess molar ratio of methanol to oil of 30:1 by using 4% NaOH as the catalyst at a reaction temperature of 55 °C. The microwave-assisted method is proven as one of the best methods of reducing the reaction time. Consequently, the amount of energy which is needed for transesterification is reduced by using this method [120].

Majewski et al. investigated the microwave assisted transesterification of corn and soybean oil for production of biodiesel using diphenylammonium salt catalysts. In this study, four types of diphenylammonium salt catalysts including tosylate (DPATs), benzenesulfonate (DPABS), mesylate (DPAMs), and chloride (DPAC) were applied and a remarkable conversion yield of approximately 100% was obtained from corn oil within 20 min. It was proved that microwave heating for around 17.5 min results in more than 80% biodiesel, while decreasing the reaction time to 15 and 10 min will reduce the conversion yield. Lastly, three diphenylammonium salt catalysts (DPATs, DPABS, and DPAMs) demonstrated a significant ability for transesterification of soybean and corn oil, and microwave-assisted systems were recognized as an efficient technology to produce biodiesel [121].

The effectual parameters including microwave irradiation power, temperature, reaction time, the molar ratio of methanol to oil, and catalyst concentration were optimized by Zu et al. The maximum yield of 96% from the oil of yellow horn (*Xanthoceras sorbifolia* Bunge) was obtained under optimal microwave-assisted method conditions of microwave irradiation power of 500 W at a temperature of 60 °C for 6 min, 1% wt catalyst, and a 6:1 (v/v) molar ratio of methanol/oil [122].

Yaakob et al. reported the microwave-assisted transesterification of *Jatropha* oil and waste frying palm oil in the presence of methanol and NaOH as the alcohol and catalyst, respectively. In this study, the effect of some critical parameters such as quality of catalyst and reaction temperature and time was investigated. The best yield conversion for *Jatropha* (89.7%) and waste frying palm oil (88.63%) was observed using 1% catalyst, a 12:1 M ratio of alcohol to oil, and a reaction temperature of 65 °C for 7 min and it was concluded that the microwave irradiation technique reduced the reaction time and temperature significantly. The biodiesel produced was tested according to European Union draft standards [123].

Microwave irradiation was used to enhance the preparation of FAME from castor oil using an absorption solid acid catalyst (H_2SO_4/C) by Yuan et al. The results indicated a significant improvement in biodiesel production using microwave heating in the presence of H_2SO_4/C as the catalyst in comparison with conventional heating. The best reaction condition for obtaining a 94 wt% FAME conversion yield was a reaction temperature of 338 K, a 12:1 M ratio of methanol to castor oil, and 5 wt% of H_2SO_4/C to castor oil as the catalyst during 60 min reaction time under 200 W microwave exit power [124].

Nogueira et al. reported the microwave-assisted production of biodiesel from macauba (*Acrocomia aculeata*) oil in the presence of ethanol and two enzyme catalysts, namely Novozyme 435 and Lipozyme IM, using statistically designed experiments. Reaction time, temperature, and enzyme loading were varied during the experiments. The temperature was not a critical parameter

according to the results, while reaction time and enzyme loading played important roles in the biodiesel production and both affect the reaction rate negatively. In addition, the results showed that microwave irradiation increased the activity of biocatalysts, reduced the time taken, and increased the yield of biodiesel [125].

Recently Rathana et al. investigated the effect of catalyst concentration, molar ratio of alcohol to oil, reaction temperature, and reaction time by using two-step transesterification assisted by microwave irradiation from kenaf seed oil. The optimum conversion of about 94% was obtained at the optimum reaction conditions of 0.55% KOH as the catalyst and a 4.5:1 M ratio of methanol to oil at 57.5 °C for 6.5 min [126].

The production of biodiesel from *Pongamia pinnata* non-edible oil under batch microwave irradiation was studied by Kamath et al. Due to the high percentage of free fatty acid in this oil, a two-step method seems to be a better approach. The conversion yields in one-step and two-step approaches were 80% and 90%, respectively with a 10:1 M ratio of alcohol to oil and 1 wt% KOH. Using microwave irradiation accelerated the reaction and reduced the reaction time to 4–5 min. Besides, the separation time was decreased by at least 90% in comparison with the conventional method. In this study, the costs of feedstock and processing were reduced by synthesis of *P. pinnata* biodiesel under microwave irradiation in order to find a cost effective and faster technology [127].

Sherbiny et al. compared the preparation of biodiesel from *Jatropha* oil using conventional and microwave irradiation methods. The optimum reaction conditions obtained from conventional heating were applied to the microwave irradiation technique. The results indicated that the best conversion yield of 99.8% from conventional heating was obtained using a 7.5:1 M ratio of methanol to oil and 1.5% KOH as the catalyst at a reaction temperature of 65 °C in 60 min. On the other hand, a 97.4% conversion yield was obtained by using the microwave irradiation technique under the same reaction conditions for 2 min. In fact, the reaction time decreased from 150 min with conventional heating (90 min for the pretreatment process and 60 min for transesterification) to only 2 min with the microwave irradiation technique. Besides, it was proved that this methodology allows the use of high free fatty acid content feedstock like *Jatropha* oil for biodiesel production [128].

A two-step transesterification process of crude palm oil with high free fatty acid content using microwave irradiation was investigated by K. Suppalakpanya et al. The optimum conditions for esterification were investigated by parametric study of the amount of alcohol, amount of catalyst, reaction time, and microwave power. The high percentage of FFA was reduced from 7.5 wt% to 2 wt% by esterification of crude palm oil using the optimum reaction condition of 4% wt/wt. H_2SO_4/FFA as the catalyst and a 1:24 M ratio of FFA to ethanol for 60 min under 70 W microwave exit power. In comparison with conventional heating under the same reaction conditions, the reaction time was decreased by 180 min. In the second step, the transesterification of esterified palm oil was carried out by using 1.5 wt% KOH as the catalyst and a molar ratio of crude palm oil to ethanol of 1:4 for 5 min under 70 W microwave irradiation. A conversion yield of 80 wt.% was obtained from a two-step esterification and transesterification process with 97.4 wt% ester content [129].

The same researchers, Suppalakpanya et al., carried out the transesterification of esterified crude palm oil with 1.7 wt% FFA under microwave irradiation. A conversion yield of 85% was obtained by using 1.5 wt% of KOH/oil and an 8.5:1 M ratio of ethanol to oil for 5 min under 70 W microwave exit power [130].

Transesterification of yellow horn oil to biodiesel by using heteropolyacid (HPA) solid catalyst was carried out under microwave irradiation by Su Zhang et al. The highest percentage yield of 96.22% was obtained with the following optimal reaction

conditions: a reaction temperature of 60 °C, a 12:1 M ratio of methanol to oil, and 1% (w/w of oil) HPA catalyst for 10 min. The result indicated that $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ had a higher efficiency when microwave irradiation was used compared with conventional heating [131].

Kanitkar et al. transesterified the rice bran and soybeans into ethyl and methyl esters by using a batch microwave system in order to compare these two types of alcohol in terms of yields, quality, and reaction kinetics. The other variables in this study were time (5, 10, 15, and 20 min) and temperature (60, 70, and 80 °C). It was observed that normally using microwave technology for both alcohols reduced the reaction time and catalyst demand in comparison with conventional heating, although ethanol required higher alcohol to oil molar ratios than methanol. In this study it was found that ethanol has some environmental, whereas methanol is better in terms of cost and performance [132].

Daeho Kim et al. investigated the use of pulsed microwave irradiation to accelerate the esterification of free fatty acid by using a heterogeneous catalyst. A 400 Hz square-pulsed microwave with a 10%–20% duty cycle and the same energy as a continuous microwave was used in this research. The results demonstrated a significant improvement in conversion yield from 39.9% to 66.1% after 15 min in comparison with the continuous microwave under the same conditions. This study showed that pulsed microwaves with repetitive strong power can improve biodiesel production even better than a low power continuous microwave [133].

M. Zahir et al. used a methanol to oil molar ratio of 10:1 and 1.0% sodium hydroxide (NaOH) as the catalyst in the transesterification of safflower (*Carthamus tinctorius* L.) under microwave irradiation. In this study, a 98.4% conversion yield was achieved at 6 min. All the biodiesel and safflower properties were compared to ASTM and EN biodiesel standards. It was concluded that the reduction in reaction time decreased the energy consumption of biodiesel production [35].

Direct production of biodiesel from microalgae biomass of *Nannochloropsis* by microwave and ultrasound radiation was reported by Koberg et al. It was found that the use of a biotechnology-based environmental system in this study to cultivate the microalgae reduced the cost of algae production significantly. Besides, microwave and ultrasound radiation with the aid of SrO catalyst were compared to identify the most effective technique. It was observed that a direct transesterification reaction using microwave irradiation resulted in a higher biodiesel yield of 37.1% in 5 min, while only 20.9% yield can be obtained in the same reaction time by using the sonication technique [134].

$\text{K}_2\text{SiO}_3/\text{C}$ is a solid base catalyst which was used in the transesterification of soybean oil under microwave irradiation by Wang Jianxun et al. The effect of some reaction parameters such as the molar ratio of methanol to oil, catalyst loading, and reaction time were investigated for conventional and microwave irradiation heating. A conversion yield of 96.5% was obtained by the conventional heating method at 65 °C with a 30:1 methanol to oil molar ratio and 24 wt% catalyst concentration after a reaction time of 2.5 h, while 96.7% yield was obtained in a reaction time of 1.5 h under the same reaction conditions by the microwave irradiation method. It was concluded that the microwave irradiation method reduced the reaction time by one hour and $\text{K}_2\text{SiO}_3/\text{C}$ has a good microwave absorption ability which increases the reaction energy efficiency and makes the reaction time shorter [135].

The experimental studies and simulations were conducted to investigate the effect of microwave irradiation on the production of biodiesel by Asakuma et al. In this study triolein, methanol, and KOH were used as the substrates. Two set of experiments were performed and in both the reaction mixture was stirred at

400 rpm. In the first set, triolein was preheated using microwaves at several irradiation times (1, 5, 10, and 20 min) and 20 W microwave exit power; then it was mixed with methanol and the reaction was done without microwave irradiation. In the second set, the methanol and triolein were preheated by conventional methods and then mixed and irradiated during the reaction time. In this research microwave irradiation was recognized as an effective method not only for transesterification but also for the preheating process [136].

Microwave-assisted transesterification of *Pongamia pinnata* was carried out using methanol as the alcohol and two types of alkaline catalyst, NaOH and KOH. An alcohol to oil molar ratio of 6:1 and a reaction temperature of 60 °C were applied to perform the experiments. The effects of reaction time (3, 5, 7, and 10 min) and catalyst concentration (0.5%, 1%, and 1.5% (w/w)) were investigated in this study. The results indicated that 0.5% (w/w) NaOH and 1% (w/w) KOH were the optimum catalyst concentrations. Biodiesel yields of 97.5% and 96.0% were obtained using 1.0% (w/w) KOH for 10 min and 0.5% (w/w) NaOH for 5 min, respectively at 60 °C. The fuel properties for all the reaction conditions were investigated and it was found that all of the biodiesels produced under the different reaction conditions met the ASTM standards for biodiesel. A significant reduction in the reaction time from 3 h using conventional heating to only 5–10 min was achieved by using microwave irradiation, which means a considerable production cost saving [137].

Hsiao et al. investigated the microwave-assisted production of biodiesel from soybean using nanopowder calcium oxide (nano CaO). The studied critical parameters were the molar ratio of alcohol to oil (6:1, 7:1, 8:1, 9:1, and 10:1), reaction time (15, 30, 45, 60, and 75 min), catalyst amount (1.0, 2.0, 3.0, 4.0, and 5.0%) and reaction temperature (323, 328, 333, 338, and 343 K). The best conversion yield (96.6%) was obtained from the following reaction conditions: a molar ratio of alcohol to oil of 7:1, 3.0 wt% of catalyst, a reaction temperature of 338 K, and a reaction time of 60 min. The results indicated that, firstly, microwave irradiation is more efficient in comparison with conventional methods and, secondly, nanopowder calcium oxide (nano CaO) is very efficient for biodiesel production from soybean oil. All the biodiesel produced in this study met the EN-14214 standards [138].

Manco et al. used a MARS 5 microwave which delivers about 1600 W of microwave energy at 2450 MHz frequency for biodiesel production from sunflower oil. Different types of pebbles (glass beads, ceramic pieces, and carborundum) were applied to perform the experiments in the presence of methanol and KOH. The obtained results showed that using microwave irradiation and carborundum significantly decreased the reaction time from 540 s (without using pebbles) to 90 s. In fact, the use of carborundum allows the set temperature to be reached in 90 s while 360 and 420 s are required when using glass beads and ceramic pieces, respectively. A gas chromatography test was carried out for quantitative analysis of the final product, and it was observed that most of the produced products were different types of methyl esters [139].

Microwave-accelerated esterification of free fatty acid with a heterogeneous catalyst to show the microwave energy efficiency was studied by Daeho Kim et al. The best conversion yield of 90% was achieved by 20 min of microwave heating with a 20:1 M ratio of alcohol to oil at a reaction temperature of 60 °C using 5 wt% sulfated zirconia as the catalyst, while the same reaction needed 130 min when using conventional heating. In this study it was found that due to the significant reduction in reaction time, the electric energy consumed by microwave heating was only 67% of the minimum conventional estimated heat energy [140].

The method of preparation of biodiesel from an inexpensive domestic microwave oven from soybean and waste cooking oil using SrO catalyst was investigated by Koberg et al. The

combination of microwave irradiation and SrO as a catalyst demonstrated excellent results. A conversion yield of 99.8% was obtained from cooked oil under 1100 W microwave exit power after 10 s. The effect of the amount of catalyst, type of catalyst, and mixing intensity was studied. A comparison between SrO and KOH showed a very high yield using SrO as a catalyst rather than KOH. In addition, magnetic stirring increased the yield from 93.2% to 99.4% under the same reaction conditions. Finally it was found that cooked oil has the potential to be a replacement for soybean oil to reduce the cost of feedstock and production as well [141].

Patil et al. used a response surface method (RSM) to obtain the optimum reaction conditions of dry algal biomass microwave-assisted extraction and transesterification. The effect of critical parameters such as dry algae to methanol (wt/v) ratio, catalyst concentration, and reaction time was analyzed by the RSM method. It was found that the optimal reaction conditions in this study were a 1:12 ratio of dry algae to methanol (wt/vol), catalyst concentration of 2 wt%, and 4 min reaction time. In conclusion, well-designed experimental runs demonstrated that the effect of microwave irradiation was a high degree of extraction and efficient conversion of oil to biodiesel [142].

The same researchers, Kamath et al., investigated two-step karanja biodiesel synthesis using the microwave technique. In the first step, the free fatty acid of crude karanja oil was reduced from 8.8% to 1.11% under 180 W microwave irradiation for 190 s with a 33.83% (w/w) methanol to oil ratio and 3.73 (w/w)% H₂SO₄. The predicted FAME yield of 91.4% was confirmed by applying 1.33 (w/w)% KOH concentration and a 33.4 (w/w)% methanol to oil ratio for 150 s reaction time at 180 W. It was concluded that the microwave technique has a significant effect on transesterification and esterification reactions [143].

The method of continuous transesterification of soybeans by using microwave irradiation was investigated by Encinar et al. The microwave flow system used in this study is shown in Fig. 11. In this study the effect of some critical reaction parameters such as temperature (50–110 °C), molar ratio of methanol to oil (3:1, 6:1, 9:1, and 12:1), and catalyst concentration (0.5%, 1.0%, and 1.5% in weight of KOH) was explored. Over 99% conversion of methyl ester was obtained with a 12:1 M ratio of methanol to oil, 1.0% catalyst concentration, and final temperature of 70 °C (2 min reaction time at 200 W microwave exit power). A comparison was made between the microwave irradiation technique and conventional heating systems and it was observed that the microwave irradiation technique was more efficient for the transesterification reaction because it gave the same conversion yield in a shorter time [144].

Surface response methodology was used in two-step microwave-assisted transesterification of Jatropha oil by Chien and Tsair. It was proved that the ratio of methanol to oil, amount of catalyst, and flow rate have a significant influence on conversion

yield and the transesterification process. In the first step, the high FFA of Jatropha oil (8.17%) was neutralized by using sulfuric acid and then NaOH was used as the catalyst in the second step. The optimum reaction conditions based on surface response methodology were a 10.74:1 M ratio of methanol to oil and 1.26 wt% catalyst concentration with a flow rate of 1.62 mL/min. The predicted conversion yield of biodiesel under the optimum conditions was 99.63% and an experimental conversion yield of 99.36% was obtained [145].

F. Motasemi and Ani. F.N investigated the microwave-assisted transesterification of waste cooking oil. A domestic microwave oven was modified to perform the experiments. The reaction conditions were a 1:4 (v/v) methanol to oil ratio, 2 wt% KOH as the catalyst at different reaction times (5, 7, and 9 min), and different microwave exit powers (100, 180, and 300 W). The best conversion yield of 81% was achieved by using 300 W of microwave exit power for 9 min at 128 °C. A comparison between microwave heating and microwave-assisted methods proved a significant decrease in reaction time from 60 to 180 min with conventional heating to 5 to 9 min with microwave-assisted transesterification [146].

Perin et al. presented the microwave-assisted transesterification of castor bean oil by using methanol or ethanol. Al₂O₃ and SiO₂ were introduced as the best basic and acidic alcoholysis catalysts for castor oil. In addition, it was observed that the catalytic system of SiO₂/50% H₂SO₄ and Al₂O₃/50% KOH can be used again for several cycles. The selected reaction conditions were a 6:1 M ratio of alcohol (methanol/ethanol) to oil and 10% w/w catalyst (acidic silica/basic alumina) in relation to castor oil mass. Satisfactory yields were obtained using H₂SO₄ immobilized in SiO₂ and methanol under conventional conditions (60 °C for 3 h) or microwave irradiation (30 min), while under basic catalysis the reaction occurred under the following conditions: (Al₂O₃/50% KOH) using methanol and conventional heating (60 °C, stirring, 1 h) as well as using microwave conditions for 5 min. From the comparison of conventional and microwave-assisted heating it was found that microwave irradiation can reduce the reaction time from many hours to a few minutes [147].

The method of biodiesel production from yellow horn (*Xanthoceras sorbifolia* Bunge.) seed oil using microwave assisted transesterification was studied by Ji Li et al. The effect of reaction temperature, molar ratio of methanol to oil, amount of catalyst, and reusability of catalyst were investigated according to the experimental design. A high conversion yield of 96% was obtained using microwave heating and alkaline anion exchange resin (heterogeneous catalyst) was recognized as a green, effective and economic technology for preparation of biodiesel in industry. The quality and composition of produced biodiesel were checked by GC-MS [148].

Prafulla D. Patil et al. compared direct microwave irradiation technique and supercritical method for transesterification of algal biomass. The response surface methodology (RSM) was applied for designing the experiment runs and optimizing the process parameters such as molar ratio of alcohol to dry/wet biomass, reaction time and temperature, and catalyst concentration. Dry and wet algal biomass was used as feedstock in microwave-assisted transesterification and supercritical methanol process, respectively. It was observed that microwave technique improved the yield and reduced the reaction time while decreased the consumed energy for separation and purification. FT-IR and TGA analysis methods were applied for quality comparison of these two techniques and it was concluded the non-catalytic supercritical methanol method produces higher quality biodiesel with better thermal stability [149].

Kang-Shin Chen et al. introduced microwave technique and waste cooking oil as two effective ways to reduce the biodiesel production cost. Type of the catalyst, catalyst concentration, molar ratio of methanol to oil, reaction time, and microwave exit power are some effectual factor which were investigated by these researchers. The best reaction condition to get 97.9% yield was

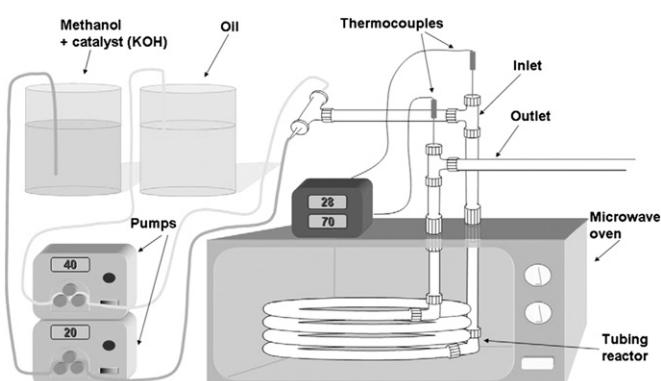


Fig. 11. Microwave flow system.

methanol to oil molar ratio of 6:1, 3 min reaction time, 750 W microwave exit power, in the presence of 0.75 wt% CH_3ONa as the catalyst. The obtained results indicated that waste cooking oil has a high potential for biodiesel production and microwave technique is one of the best methods to improve the yield and reduce the reaction time which both lead to a lower production cost [150].

P. Khemthong et al. reported the CaO derived from eggshell wastes as the heterogeneous catalysts for biodiesel production of palm oil under microwave heating system. The effect of reaction time, molar ratio of alcohol to oil, catalyst loading, and microwave exit power were investigated in this study. The experimental results showed a high biodiesel production yield of 96.7%. The optimal reaction condition for maximum yield were 4 min reaction time, 18:1 M ratio of alcohol to oil, 15% catalyst loading, under 900 W microwave exit power. It was concluded that CaO derived from eggshell wastes has a high potential to be used as the catalyst for microwave irradiation production of biodiesel [151].

5. Variables affecting the transesterification reaction

The yield of biodiesel is affected by some critical parameters in the transesterification reaction. In order to obtain the maximum conversion yield, these variables should be optimized. The most important variables in the transesterification reaction are reviewed in Refs. [2,16,22,152,153] and are listed below.

- FFA of the oil
- Moisture and water content in the oil
- Reaction temperature
- Reaction time
- Molar ratio of alcohol to oil and type/chemical structure of alcohol
- Catalyst type and concentration
- Mixing intensity (stirring)
- Use of organic co-solvents

6. Sustainability of microwave-assisted biodiesel production systems

In this section, a simple microwave-assisted transesterification system for biodiesel production is assumed as a case study to calculate the energy payback of the system. In order to do this, electrical energy usage for production of 1 kg biodiesel using microwave irradiation technique and the potential electricity production of the same quantity of produced biodiesel are calculated.

According to F. Motasemi and Ani. F. N [146], an average microwave exit power of 300 W, for at least 9 min with mixing intensity of 300 rpm are required for 81% yield of biodiesel. Thus, the consumed energy for each batch will be the multiplication of 300 W by 9 min. This calculation is illustrated in Eq. (1).

$$\text{MEC} = 300(\text{Watts}) \times 9(\text{min}) \times \left(\frac{1 \text{ hour}}{60 \text{ min}} \right) = 45(\text{Watt-hours}) \quad (1)$$

On the other hand, microwave was equipped by a mechanical stirrer which it consumes energy as well. The maximum electricity consumption by the stirrer in this study was 90 W. Thus, the stirrer energy consumption which is the summation of transesterification and washing process was calculated as follows in Eq. (2).

$$\begin{aligned} \text{SEC} &= 90(\text{Watts}) \times \left[(9(\text{min(transesterification)})) \right. \\ &\quad \left. + 5(\text{min(washing)}) \times \left(\frac{1 \text{ hour}}{60 \text{ min}} \right) \right] \\ &= 21(\text{Watt-hours}) \end{aligned} \quad (2)$$

The total energy consumption by this system will be the summation of MEC and SEC. Eq. (3) shows the total energy consumption in each batch.

$$\text{TEC} = \text{MEC} + \text{SEC} = 45 + 21 = 66 \text{ (Watt-hours)} \quad (3)$$

This amount of energy was used for production of 162 mL biodiesel. Thus, the total energy consumption for production of 1 l biodiesel can be calculated as it is shown in Eqs. (4) and (5).

$$\begin{aligned} \text{TECPL} &= \frac{\text{TEC}}{\text{The amount of produced biodiesel}} = \frac{66(\text{Watt-hours})}{0.162(\text{Liter})} \\ &= 407.4 \left(\frac{\text{Watt-hours}}{\text{Liter}} \right) \end{aligned} \quad (4)$$

$$\text{TECPL} = 407.4 \left(\frac{\text{Watt-hours}}{\text{Liter}} \right) \times \left(\frac{1 \text{ kilo Watt-hours}}{1000 \text{ Watt-hour}} \right) = 0.4074 \left(\frac{\text{kWh}}{\text{Liter}} \right) \quad (5)$$

On the other hand, the density of produced biodiesel in the aforementioned study was 0.8703(kg/Liter), so TECPK will be:

$$\text{TECPK} = 0.4444 \left(\frac{\text{kWh}}{\text{Liter}} \right) \times \left(\frac{1}{0.8703 \left(\frac{\text{kg}}{\text{Liter}} \right)} \right) = 0.4681 \left(\frac{\text{kWh}}{\text{kg}} \right) \quad (6)$$

It shows that for the production of one kg biodiesel, 0.4681kWh electrical energy has been used in a simple microwave-assisted biodiesel production system. On the other hand, according to Chauhan BS et al. the brake specific fuel consumption (BSFC) which measures the efficiency of an engine in case of biodiesel was found to be about (average) 0.47(kg/kWh) [154]. Therefore, produced energy by using each kg of biodiesel (B100) can be calculated by using BSFC.

$$PE = \frac{1 \text{ Kg biodiesel}}{0.47(\text{kg/kWh})} = 2.1277(\text{kWh}) \quad (7)$$

Fig. 12 illustrates the energy payback of microwave-assisted biodiesel production system. As can be seen from the figure, the average of 2.1277 kWh electrical energy can be produced from one kg biodiesel, while production of one kg biodiesel needs only

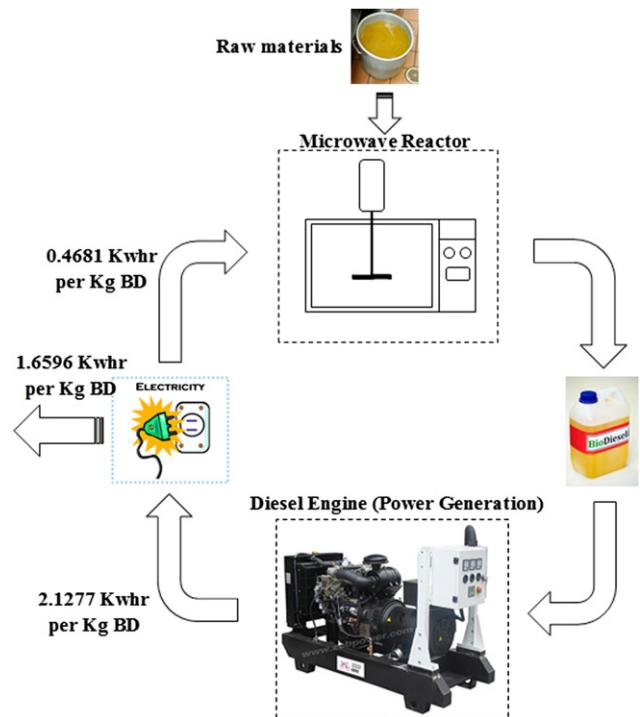


Fig. 12. Energy payback of microwave-assisted biodiesel production system.

0.4681 kWh electricity. Thus, using microwave-assisted production of biodiesel can save the energy significantly. This system has the potential for production of 1.6596 kWh extra electrical energy per kg biodiesel which it proves the sustainability of system.

7. Future directions of biodiesel

Due to awareness of the depletion of fossil fuels, which are forecasted to dry up within around 50 years, and environmental hazards caused by using these limited supplies of energy, considerable attention has been given to alternative fuels as substitutes for fossil fuels. Biodiesel is an alternative fuel for diesel engines; it is recognized as one of the most promising alternatives for world transportation needs. It has gained much attention and has become more attractive because of its environmental benefits in comparison with conventional diesel; it decreases carbon emissions to a greater extent. It is known as one of the favorable alternatives which could possibly improve energy security. It comes from renewable resources and is known as a biodegradable non-toxic fuel. Biodiesel reduces the amount of greenhouse gas emissions and emits less CO₂, SO₂, CO, HC, and PM in comparison to conventional diesel. So it is clear that the future of biodiesel is growing. One of the short-term aims of biodiesel production is to increase the demand and availability of locally produced biodiesel while the long-term aim is to have an action guide to the development of a functional biodiesel industry. In pursuing these goals, biodiesel production is facing several challenges and issues such as strong global competition, competition between food and fuel, and feedstock availability, but the most challenging issue is the price of biodiesel, which is a considerable barrier to the large-scale production of biodiesel. The cost of biodiesel depends on many factors including the availability and type of the feedstock, production technologies, additives used, and the cost of the operation. After feedstock cost, the processing cost of biodiesel represents the second largest proportion of the total biodiesel cost. The cost of the transesterification process is the main associated aspect of the biodiesel processing cost. Meeting the growing demand for biodiesel and maintaining the validity of the biodiesel industry in the long-term future require a significant reduction in the cost of biodiesel for it to be able to compete economically against fossil fuels and other alternative fuels. Thus, improving the production technologies is one of the options for reducing the production costs. It can be also an effective strategy for increasing the supply and demand of biodiesel fuel. So far research have been done on homogeneous liquid-liquid reaction, more research can be done on heterogeneous reaction using solid catalyst such as Zeolites etc. Finally, the creation of a dependable biodiesel production chain, public acceptance, cost reduction, and processing technology maturity are vital factors which can help policy makers and biodiesel industry players to establish a biodiesel market which will be sustainable in the long term.

8. Conclusions

To recapitulate, biodiesel is a potential substitute for diesel engines and the adoption of this fuel has some primary advantages such as the environmental benefits of reducing emissions and amelioration of national energy security through a reduction in the fossil fuel consumption. Apart from the short-term benefits, it has several long-term advantages especially with regard to developing technologies and the economic contribution from biodiesel production to rural communities. Development of the agricultural sector, job creation, and investment in plants are some of the other benefits. Transesterification is the most

important technique for biodiesel production. It is the well-established chemical reaction of vegetable oils or animal fats with an alcohol to form fatty acid alkyl esters and glycerol. Several techniques have been developed for biodiesel production. In these methods, the transesterification process is carried out in the presence and absence of catalyst. Water content and FFA play vital roles in the type of transesterification process selected for conversion of biomass to biodiesel. The catalyst is applied to accelerate the reaction and produce biodiesel of higher quality. The conventional heating method is the technique traditionally used to produce biodiesel, although other emerging technologies for the transesterification process such as supercritical, ultrasound-assisted, and microwave-assisted methods have been introduced in recent years. The microwave-assisted technique is reviewed in this paper as an attempt to find a way to reduce the production cost and produce a higher quality biodiesel. This method has been found to be a promising well-established technique to accelerate and enhance the transesterification reaction in comparison with conventional techniques. In addition, the different types of feedstock used for biodiesel production and the advantages and disadvantages of biodiesel are summarized in this paper. Finally, the energy payback for 1 kg produced biodiesel by microwave-assisted method in one case study is calculated. 1.6596 kWh extra electrical energy in this case can be a proof for sustainability of microwave technology.

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